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CARBON DIOXIDE ACTIVATION; FORMATION OF TRANS- (PH3P) 2RH(CO) (---ETC(U)  
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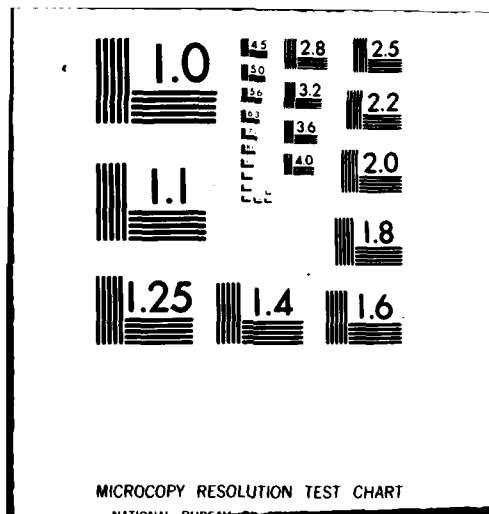
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Technical Report No. 2

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Carbon Dioxide Activation;  
Formation of trans-( $\text{Ph}_3\text{P}$ ) $_2\text{Rh}(\text{CO})(\text{OCO}_2\text{H})$  in  
the Reaction of  $\text{CO}_2$  with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3/\text{CO}$ .

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p> ↓  The intermediate produced from the interaction of  HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> with CO reacts with CO<sub>2</sub> to yield a novel bicarbonate  complex, <u>trans</u>-(PPh<sub>3</sub>)<sub>2</sub>Rh(CO)(OCO<sub>2</sub>H) (<u>1</u>) whose structure has been  established X-ray crystallographically. The bicarbonate complex  undergoes reversible loss of CO<sub>2</sub>. Results from the reaction of  DRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/CO with CO<sub>2</sub> are consistent with a mechanism for  formation of <u>1</u> involving rhodium-promoted CO<sub>2</sub> disproportionation  followed by H<sup>-</sup> transfer from Rh to O of coordinated carbonate. </p>		

Carbon Dioxide Activation; Formation of trans-(Ph<sub>3</sub>P)<sub>2</sub>Rh(CO)(OCO<sub>2</sub>H) in  
the Reaction of CO<sub>2</sub> with HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/CO.

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Summary. The intermediate produced from the interaction of HRh(CO)-  
(PPh<sub>3</sub>)<sub>3</sub> with CO reacts with carbon dioxide to yield a novel bicarbonate  
complex, trans-(PPh<sub>3</sub>)<sub>2</sub>Rh(CO)(OCO<sub>2</sub>H)(I), whose structure has been  
established X-ray crystallographically; I undergoes reversible loss of  
CO<sub>2</sub>.

The search for alternative fuels and chemical feedstocks has stimulated  
considerable interest in the activation of carbon oxides by transition  
metals. While there exists a long-standing and rich chemistry of  
coordinated carbon monoxide, the coordination chemistry  
of carbon dioxide is largely unknown.<sup>1</sup> We report herein a novel  
bicarbonate complex, (Ph<sub>3</sub>P)<sub>2</sub>Rh(CO)(OCO<sub>2</sub>H)(I), produced via a previously  
unrecognized pathway from the reaction of CO<sub>2</sub> with HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>/CO.

When a yellow benzene solution of HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Rh<sub>2</sub>(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>  
(formed by pretreatment of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> with CO<sup>2</sup>) was stirred for  
ca. 36 hr under an atmosphere of pure CO<sub>2</sub> at 5°C, the solution slowly

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IR(KBr): 1970(s), 1600(m), 1500(m), 1350(m); NMR(CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.25(bm).

Crystal data: (I)  $C_{38}H_{31}O_4P_2Rh \cdot 2 CH_2Cl_2$ ,  $M = 886.4$   
triclinic, space group  $P\bar{1}$ ,  $a = 12.702(2)$ ,  $b = 14.736(2)$ ,  $c = 11.582(2) \text{ \AA}$ ,  
 $\alpha = 99.46(1)$ ,  $\beta = 107.56(1)$ ,  $\gamma = 98.258(1)^\circ$ ,  $V = 1995.2 \text{ \AA}^3$ . All  
X-ray measurements were carried out on a Syntex P2<sub>1</sub> autodiffractometer  
(MoK $\alpha$  radiation, graphite monochromator), where the crystal was  
maintained at  $-100^\circ\text{C}$  in a dry  $N_2$  stream. The unit cell contains two  
molecules of  $CH_2Cl_2$  of solvation. Using 6473 reflections with  $I_o > 3.0\sigma_{I_o}$ ,  
the structure was solved by conventional heavy-atom methods and refined  
to final R and wR values of 0.040 and 0.043, respectively. Refinement  
included treatment of phenyl rings as rigid groups, but independent  
refinement of all other parameters, including those of the solvent  
hydrogen atoms.<sup>†</sup>

† Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB11EW. Any request should be accompanied by the full literature citation for this communication.

The molecular structure (Figure) consists of a square planar arrangement of trans-triphenylphosphines, CO, and bicarbonate ligands about Rh; the five atoms Rh, P1, P2, C1, O2 are coplanar to within 0.01Å. The bicarbonate plane, (also  $\pm 0.01\text{\AA}$ ) makes an angle of  $85.2^\circ$  with the metal coordination plane compared with  $73^\circ$  in (bicarbonate)-methyl-trans-bis(triethylphosphine)palladium(II).<sup>4</sup> Pairs of molecules are hydrogen bonded through the bicarbonate ligands across crystallographic inversion centers, in a manner similar to the afore-mentioned Pd(II) complex, except that in I the C-O distances (Figure) are significantly different, the bicarbonate hydrogen being attached to the oxygen with the longest C-O bond.<sup>‡</sup>

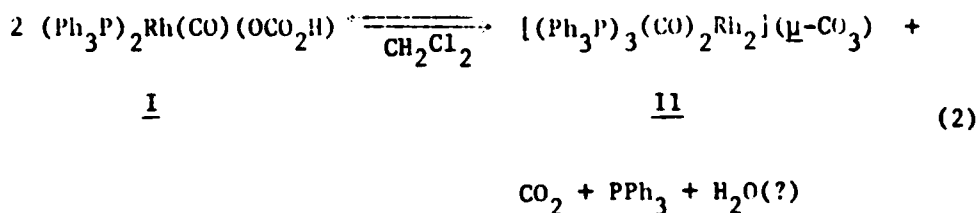
Regarding the mechanism leading to I, especially the origin of the bicarbonate ligand, the major pathway leading to I apparently does not involve adventitious moisture as demonstrated by the following observations: 1) neither intentional addition of  $\text{H}_2\text{O}$  to the reaction medium nor scrupulous drying of all materials and glassware had any significant effect on the yield or rate of formation of I; 2) starting with  $\text{DRh}(\text{CO})(\text{PPh}_3)_3$  (ca. 66 atom %), product I was obtained, substantially deuterium-enriched (ca. 33 atom %, calculated from  $\text{H}_2\text{O}/\text{D}_2\text{O}$  ratio produced on pyrolysis).<sup>§</sup> These results are consistent with a mechanism

<sup>‡</sup> The formation of  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{OCO}_2\text{H})$  from  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{OH}$  and  $\text{CO}_2$  has been mentioned in two earlier reports. The IR spectrum of our authentic I is identical to the compound prepared by Otsuka and Ibers,<sup>5</sup> but at variance with Vaska's product,<sup>6</sup> the formulation of which has been questioned.<sup>5</sup>

<sup>§</sup> No D/H exchange was observed between  $\text{DRh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{H}_2\text{O}$  in benzene at  $20^\circ$  over a few hours.

involving initial rhodium-promoted reductive disproportionation of  $\text{CO}_2$ <sup>7,8</sup> followed by H-transfer from Rh to O of coordinated carbonate (Scheme I). Our preliminary attempts to isolate the red suspected precursor to I (possibly a hydrido- $\text{CO}_2$  or hydrido-carbonate species) have resulted in rapid conversion, even in the solid state, to I.

While solutions of I in  $\text{CO}_2$ -saturated  $\text{CH}_2\text{Cl}_2$  are stable at  $0^\circ$  for several hours, under an atmosphere of argon I is rapidly converted with loss of  $\text{CO}_2$ ,  $\text{PPh}_3$  and  $\text{H}_2\text{O}(?)$  to a new material II (IR: 1970(s), 1502(s), 1190(m)  $\text{cm}^{-1}$ ;  $\text{Ph}_3\text{P/Rh}$  ca. 1.5). Interestingly, pyrolysis of II still produced  $\text{CO}_2$  (1  $\text{CO}_2$ /2 Rh/3  $\text{PPh}_3$ ) and II was reconverted to I in the presence of  $\text{CO}_2$ ,  $\text{PPh}_3$ , and  $\text{H}_2\text{O}$  (eq. 2). Based on these results we tentatively formulate II as a binuclear carbonate complex,  $(\text{PPh}_3)_2(\text{CO})\text{-Rh}(\mu\text{-CO}_3)\text{Rh}(\text{CO})(\text{PPh}_3)$ .<sup>§§</sup>



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§§ A similar decomposition mode has been postulated for the corresponding  $(\text{R}_3\text{P})_2\text{Rh}(\text{CO})\text{OCO}_2\text{H}$  complexes (R = cyclohexyl, 1-propyl).<sup>5</sup> The related perphosphinated derivative,  $\text{Rh}_2(\text{PPh}_3)_5(\mu\text{-CO}_3)$ , is known<sup>6</sup> ( $\nu_{\text{CO}}$ , 1485, 1465  $\text{cm}^{-1}$ ).



Foundation for the purchase of the Syntex P2<sub>1</sub> diffractometer and an NSF Undergraduate Research Participation award (C.L.T.).

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Scheme I

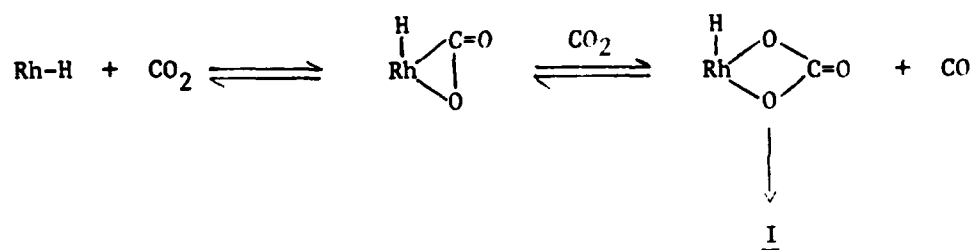


Figure Caption:

A view of the structure of I. Principal bond lengths ( $\text{\AA}$ ): Rh-C1 = 1.798(4), Rh-P1 = 2.333(1), Rh-P2 = 2.332(1), Rh-O2 = 2.075(2), O2-C2 = 1.283(4), C2-O3 = 1.243(4), C2-O4 = 1.336(4). Principal bond angles ( $^{\circ}$ ): C1-Rh-P1 = 89.1(1), C1-Rh-P2 = 91.8(1), O2-Rh-P1 = 90.4(1), O2-Rh-P2 = 88.7(1), Rh-O2-C2 = 118.6(2), O2-C2-O3 = 124.8(3), O2-C2-O4 = 113.2(3), O3-C2-O4 = 122.0(3).

